Development of Guidelines for Contaminated Soil and Groundwater at U.S. Army Installations

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ABSTRACT

There is a requirement to develop environmental guidelines for materials which contaminate the soil of Army installations as a result of past activities and which may present a hazard off post due to migration in the groundwater or otherwise. The U.S. Army Medical Bioengineering Research and Development Laboratory has taken a total ecological approach to development of guidelines in evaluating the hazard of contaminants to humans, wildlife, aquatic life, vegetation and domestic animals. Sufficient data have been generated for diisopropyl methylphosphonate and dicyclopentadiene to recommend temporary guidelines for food, drinking water, and water for irrigation, recreation and aquatic life.

TWO KINDS OF OPERATIONS fall within the Army definition of installation restoration. The first concerns preparation of an Army installation for release to a civilian agency, while the second concerns cleanup of an installation not necessarily intended for release, but which presents an off-post hazard by reason of activities carried out in the past. The responsibility of the Army in the first case is to make certain that no materials remain on post which would present a hazard in terms of the new use, while in the second case the responsibility is to prevent any material generated as a result of former activities from becoming an environmental hazard off post. The U.S. Army Medical Bioengineering Research and Development Laboratory (BRDL) became involved in environmental criteria in 1975 when Rocky Mountain Arsenal (RMA) was designated for restoration. Prior to 1957, RMA was a manufacturing site for chemical warfare agents, and more recently the Arsenal has carried out chemical destruction of those stocks. A pesticide manufacturer is a tenant of the post, and in the past the Army has been responsible for the tenant's wastewater. Some of the wastes from these various operations have been discharged into shallow, lined and unlined ponds. In 1974, chemical contaminants were found to be migrating off post in groundwaters of the Arsenal.

PROCEDURES

As the first step, BRDL performed a problem definition study on 16 materials (Table 1) known to be present in the soil and groundwater of the Arsenal by reason of a preliminary sampling program, or indicated to be present because of the operational history of the post. Subsequent problem definition studies (Table 2) are based on contaminants detected in groundwater by the Materials Analysis Laboratory at RMA and the Chemical Systems Laboratory at Aberdeen Proving Ground, Md. A problem definition study is a document review which has the following purposes:

(1) to establish a data base of physical, chemical and biological properties of the suspected contaminant;

(2) to establish a site-specific data base of materials relating to the history of the contaminant at the post, including production, storage, consumption and disposal, as well as analytical data and all available information on the geohydrology of ground and surface waters at the post;

(3) to identify potential health hazards, particularly those affecting personnel engaged in soil and water sampling and restoration activities;

(4) to compute, where possible, provisional pollutant limit values for soil and water (1),

(5) to compile a list of deficiencies in the data base.

Table 1 - Suspected RMA Contaminants (2)

From Army Activities	From Tenant Activities
Diisopropyl methylphosphonate	Dicyclopentadiene
Isopropyl methylphosphonic acid	Aldrin
Methylphosphonic acid	Dieldrin
Mustard	Endrin
Thiodiglycol	Chlordane
Lewisite	
Lewisite oxide	
Arsenic compounds	
Mercury compounds	
Chlorate salts	
Wheat rust	

Table 2 - RMA Groundwater Contaminants

1,4-Dithiane
1,4-Thioxane
Isodrin
Tetrachloroethylene
Tetrachlorobenzene
Trichloroethylene
Hexachloronorbornadiene
Hexachlorobutadiene
1-Chloro-2,3-dibromopropane (Nemagon)
7-Hydroxybicyclo [2.2.1] hepta-2,5-diene
p-Chlorophenyl methyl sulfide (3)
p-Chlorophenyl methyl sulfoxide (3)
p-Chlorophenyl methyl sulfone (3)
Benzene (3)
Toluene (3)
Xylene (3)
Chloroform
Methylene chloride
Triethylphosphate

Early in the program it became clear that a formal coordination mechanism would be necessary to assure that the data developed in support of standards would be acceptable to the scientific community as well as the Federal agencies concerned. For this purpose, the National Academy of Sciences and National Research Council have established, under the existing Committee for Military Environmental Research, a Subcommittee for Land Renovation, which reviews all materials generated in the course of standards development and advises BRDL on the need for further work. The Environmental Protection Agency, Dept. of Health, Education and Welfare, Dept. of Agriculture and Dept. of Interior have designated representatives who attend Subcommittee meetings and who also review data developed by BRDL. In addition, we rely on expert consultants from outside the defense community.

We have endeavored to maintain a total ecological approach to standards development, with studies on indigenous species as well as laboratory animals. For most requirements research protocols have been prepared in-house with the aid of consultants, then submitted for approval to the National Academy Subcom-

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mittee and the Federal agencies. About a year after toxicology studies have been initiated for any particular compound, we are in a position to go before the Subcommittee and the Federal agencies and recommend temporary guidelines to protect most categories of water consumers.

Current mammalian protocols are outlined in Table 3. The first year's work comprises standard acute and subacute assays with special tests (such as demyelination) included where appropriate. Ames tests are included in the mammalian protocols because it is desirable to have these tasks performed concurrently. The selection of chronic tests is based in part on the results of previous tests. We have taken the position that a negative mutagenesis assay will preclude the necessity for long-term carcinogenesis studies unless evidence of cancer appears in other tests. Cattle have been included in the mammalian studies both for their own protection and for the protection of consumers. Determination of acute toxicity is followed by six-month feeding experiments and reproduction studies if results from laboratory animal experiments suggest potential toxic hazards. Bioaccumulation and excretion studies are designed to insure that humans are not subjected to risk through exposure to the contaminant or its metabolites through the milk or meat of cattle.

Table 3 - Mammalian Toxicology Protocol

Test	Test Animal
Phase I	
Acute oral LD50	Rat
Acute dermal LD50	Rat
Eye and skin irritation	Rabbit
Skin sensitization	Guinea Pig
Metabolism	Rat, dog or monkey
Microbial mutagenesis (Ames)	
Phase II	
90-Day feeding	Rat, mouse
14-Day feeding	Dog or monkey
Liver enzyme induction	Rat
Dominant lethal	Rat
Phase III	
3-Generation reproduction	Rat
Carcinogenesis	Rat, mouse
Teratology	Rat, rabbit
Detailed metabolism	Rat, dog, monkey
180-Day feeding	Dog

For wildlife our first concern has been selection of appropriate species. Species indigenous to RMA would be preferred, but it is more important that there be an adequate data base concerning rearing, feeding and dosing each species in captivity. It is also desirable that species chosen represent a range of taxa and occupy different positions in the food chain. The Environmental Protection Agency encourages selection of the mallard and bobwhite for pesticide studies. In addition we have chosen the mink as top-of-food-chain representative, although it is not indigenous to RMA, because there is an adequate data base, and the mink is known to be sensitive to food contaminants. As in the case of domestic animal studies, the wildlife protocol addresses two concerns; protection of wildlife and protection of humans consuming possibly contaminated wildlife. Rangefinding and LD50 determination are followed by 5 or 21 day dietary studies. Chronic studies overlap a period of reproduction for all species. Bioaccumulation and excretion studies for birds involve dose administration both by feeding and by gastric lavage.

The decision to carry out aquatic toxicity studies is based on the potential for a contaminant to migrate to off-post surface waters. Aquatic tests are conducted at different phylogenetic levels. The first phase aquatic studies involve static bioassays; 96 hour LC50's for four fish species (bluegill, rainbow trout, fathead minnow and channel catfish), 48 hour EC50's for invertebrates (scud, water flea, sowbug and midge) and 96 hour EC50's for algae (blue-green, green and diatom). Effects of pH, temperature and water hardness on toxicity to fish and effects of the contaminant on life stages of fish are examined. To protect the health of humans consuming fish, the bioaccumulation of contaminants is measured. If first phase tests indicate a possible toxic hazard, second phase tests are carried out under dynamic conditions for the most sensitive fish species. Acute tests are repeated, and chronic (life cycle) tests include growth, reproduction and physiological effects.

Preparation of a standard protocol for phytotoxicity is the area in which we have found least guidance in the literature. We have selected plant species with different edible parts which are important in the food chain and/or local agriculture. For RMA we have chosen wheat, sugar beet, fescue, corn, and green bean, among others. This collection provides a range of susceptibilities and includes both C3 and C4 photosynthetic types. The protocol involves initial screening of all plant species with respect to each contaminant, which may be incorporated in the soil, in the irrigation water, or in a hydroponic solution. Seed germination studies are run concurrently, and the toxicity to soil microorganisms may be examined. To assess the risk to humans consuming plant parts, bioaccumulation of the contaminant is determined using radiolabelled compounds. Dose response studies are carried out for the most susceptible species if warranted by screening results.

Environmental fate studies are conducted to evaluate hazards presented by a contaminant by reason of its soil mobility, and by reason of its conversion to other and possibly more toxic materials. Rates and products of chemical, photochemical and biochemical transformations are surveyed in water, soil and sediments, and soil translocation characteristics are examined. It is attempted to simulate field conditions as nearly as possible, but this may be constrained by analytical capabilities. Other chemistry studies involve development of methods for preparation, purification and analysis of contaminants used for toxicity tests. For these purposes BRDL has found it important to maintain a strong in-house research capability in analytical and preparative organic chemistry. Many of the chemicals under study are not commercially available, and those which are available may not be of research quality. Fractionated diisopropyl methylphosphonate (DIMP), e.g., custom synthesized by means of the Michaelis-Arbuzov reaction, contained 1-2% impurities, including diisopropyl phosphite and all possible compounds resulting from exchange of methyl and isopropyl groups in DIMP. A sample used in the Ames assay, prepared in-house by reaction of isopropyl alcohol with methylphosphonyl dichloride in the presence of pyridine, contained less than 0.1% impurities by gas chromatography.

RESULTS

Because DIMP and dicyclopentadiene (DCPD) were found in off-post RMA groundwaters in significant concentrations, and because there was almost no toxicology data base for either, BRDL initiated studies for both compounds. Selected results from the first year's mammalian studies, which have been presented elsewhere (4, 5), are listed in Table 4. Research in progress indicates that cattle and wildlife (possibly excepting the mink) are no more susceptible to intoxication by DIMP and DCPD than laboratory animals. DCPD is about 10 times more toxic than DIMP to aquatic organisms during

Table 4 - Mammalian Toxicity; Selected Results for DIMP (4) and DCPD (5)

Test	DIMP	DCPD
Oral LD50 (95% cl), mg/kg		
Rat, male	1125	520 (420-645)
Rat, female	826 (747-914)	378 (303-473)
Mouse, male	1041 (903-1201)	190 (125-289)
Mouse, female	1363 (1165-1594)	250 (170-368)
Skin irritation, rabbit		
Effect of 2g/kg	High mortality	Minimal irritation
Eye irritation, rabbit	Recovery complete	Temporary
Skin sensitization, guinea pig	Moderate	Negative
Liver enzyme induction		
4-Day dietary, rat	Positive at 3000 ppm	Negative at 750 ppm
Feeding studies no effect level, ppm		
90-Day rat	300	750
90-Day mouse	2100	273
14-Day dog	1500	375
Microbial mutagenesis (Ames)		
Without activation	Negative	Negative
Human or rat liver activation	Negative	Negative

Table 5 - Recommended Temporary Guidelines for DIMP and DCPD

Category	DIMP (ppm)	DCPD (ppm)
Food	0.5	1.3
Drinking water	0.5	1.3
Water: for recreation	5	13
Water: to protect aquatic life	12.5	0.5
Water: for irrigation	20	20

static bioassays, with 96-hour LC50's ranging from 15 to 31 mg/l for fish (6). The water flea (48-hour EC50 = 10.5 mg/l) is the most susceptible to DCPD, while the bluegill (96 hour LC50 = 257 mg/l) is the most susceptible to DIMP. Environmental effects are minor. The bluegill does not bioconcentrate DIMP, and the maximum bioconcentration factor for DCPD is 53. Analysis of phytotoxicity data is incomplete, but it appears that alfalfa, sugar beets, corn and green beans suffer a loss of yield relative to controls when irrigated with water containing DIMP at a level of 50 mg/l or more. The most common symptom is leaf necrosis. The bioconcentration factor reaches a maximum of about 11 in the leaves. DCPD is less phytotoxic than DIMP, is toxic only at levels well above its solubility limit in water, and does not bioaccumulate. Neither contaminant prohibits seed germination at levels up to 1000 mg/l.

From these results, BRDL has recommended the following temporary guidelines for DIMP and DCPD: for food and drinking water, to protect human consumers, 0.5 ppm DIMP and 1.3 ppm DCPD. These values are concurred in by the National Academy of Sciences Committee on Military Environmental Research (7). Other recommended temporary guidelines are listed in Table 5. We are still a year away from final guidelines for DIMP and DCPD. In the meantime, we have begun mammalian and phytotoxicity studies on p-chlorophenyl methyl sulfide, sulfoxide and sulfone, intermediates in the preparation of the herbicide Planavin, which have been detected in RMA groundwater. We are generally satisfied with progress made under the overall program, particularly with respect to provisions for regular review and feedback. We believe that BRDL has provided a sound program for development of restoration guidelines for application to civil as well as Defense Department problems.

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REFERENCES

1. D. H. Rosenblatt, I. Muul, J. C. Dacre, G. Woodard, T. A. Miller, and D. R. Cogley, "Soil Pollutant Limit Values," paper in preparation.

2. D. H. Rosenblatt, T. A. Miller, J. C. Dacre, I. Muul, and D. R. Cogley, "Problem Definition Studies on Potential Environmental Pollutants. II. Physical Chemical, Toxicological, and Biological Properties of 16 Substances," Technical Report 7509, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD (Dec 1975). AD A030428.

3. T. A. Miller, D. H. Rosenblatt, J. C. Dacre, J. G. Pearson, R. K. Kulkarni, J. L. Welch, D. R. Cogley, and G. Woodard, "Problem Definition Studies on Potential Environmental Pollutants. IV. Physical, Chemical, Toxicological, and Biological Properties of Benzene; Toluene; Xylenes; and p-Chlorophenyl Methyl Sulfide, Sulfoxide, and Sulfone," Technical Report 7605, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, MD (June 1976). AD A040435.

4. J. C. Dacre and E. R. Hart, "Mammalian Toxicologic Studies on Diisopropyl Methylphosphonate," Proceedings of the First International Congress on Toxicology, Toronto, Canada, 30 March - 2 April 1977, in press.

5. E. R. Hart and J. C. Dacre, "Mammalian Toxicologic Studies on Dicyclopentadiene," Proceedings of the First International Congress on Toxicology, Toronto, Canada, 30 March - 2 April 1977, in press.

6. R. E. Bently, G. A. LeBlanc, T. A. Hollister, and B. H. Sleight, III, "Acute Toxicity of Diisopropyl Methylphosphonate and Dicyclopentadiene to Aquatic Organisms," Final Report, Contract DAMD-17-75-C-5073 (July 1976). AD A037750.

7. National Academy of Sciences, "Statement of the Committee on Military Environmental Research on the Status of Research into Biological Effects of Environmental Contaminants at Rocky Mountain Arsenal," National Research Council, Assembly of Life Sciences, 2101 Constitution Ave., Washington. D.C. 20418 (Jan 1977).

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There is a requirement to develop environmental guidelines for materials which contaminate the soil of Army installations as a result of past activities and which may present a hazard off post due to migration in the groundwater or otherwise. These guidelines are needed to evaluate the degree of hazard to humans and other life forms exposed to the contaminants and to provide performance standards for water containment and treatment systems, where required. The Army Medical Bioengineering Research and Development Laboratory has taken a total ecological approach to development of guidelines in evaluating the

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the hazard of contaminants to humans, wildlife, aquatic life, vegetation and domestic animals. Research protocols and priorities have been developed through coordination with Federal agencies and the National Academy of Sciences Five known contaminants at an Army installation are presently under study. Sufficient data have been generated for two of them to recommend temporary guidelines for food, drinking water, and water for irrigation, recreation and aquatic life. Ultimately, guidelines will be developed for soil and water to protect all categories of consumers, irrespective of the modes of exposure.